UNCLASSIFIED

AD NUMBER
ADB022565
LIMITATION CHANGES

TO:

Approved for public release; distribution is unlimited.

FROM:

Distribution authorized to U.S. Gov't. agencies only; Test and Evaluation; OCT 1977. Other requests shall be referred to Chemical Systems Lab., Aberdeen Proving Ground, MD.

AUTHORITY

USARDC ltr 8 Mar 1979

THIS PAGE IS UNCLASSIFIED

AD

CONTRACTOR REPORT ARCSL-CR-77041

A STUDY ON OPTICALLY TRANSPARENT
POLYURETHANE COATINGS FOR THE
NEW PROTECTIVE MASK

by

John A. Brown

Harry S. Katz

October, 1977

D D C
RECEIVED
NOV 2 1977
F

UTILITY RESEARCH COMPANY
PO Box 107
Montclair, New Jersey 07042

Contract DAAA15-76-C-0136

ADB022565

AD No.
DDC FILE COPY

REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
ARCSL-CR-77041		

4. TITLE (and Subtitle)

A STUDY ON OPTICALLY TRANSPARENT POLYURETHANE COATINGS FOR THE NEW PROTECTIVE MASK.

5. TYPE OF REPORT & PERIOD COVERED

Final Technical Report, June 1976 — Feb 1977.

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)

John A. Brown and Harry S. Katz

8. CONTRACT OR GRANT NUMBER(s)

DAAA15-76-C-0136

9. PERFORMING ORGANIZATION NAME AND ADDRESS

Utility Research Company, PO Box 107
Montclair, New Jersey 07042

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS

11. CONTROLLING OFFICE NAME AND ADDRESS

Commander, Chemical Systems Laboratory
Attn: DRDAR-CLJ-R
Aberdeen Proving Ground, Maryland 21010

12. REPORT DATE

Oct 1977

13. NUMBER OF PAGES

22 p.

14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)

Commander, Chemical Systems Laboratory
Attn: DRDAR-CLW-P
Aberdeen Proving Ground, Maryland 21010
(CPO - Mr. J. Mok, 671-3705)

15. SECURITY CLASS. (of this report)

UNCLASSIFIED

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

NA

16. DISTRIBUTION STATEMENT (of this Report)

Distribution limited to US Government agencies only because of test and evaluation, October 1977. Other requests for this document must be referred to Director, Chemical Systems Laboratory, Attn: DRDAR-CLJ-R, Aberdeen Proving Ground, Maryland 21010.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

DDC
RECEIVED
NOV 2 1977
F

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Protective mask	Viton coating	Penetration
Individual protection	Optically clear coatings	Gel spots
Silicone rubber	Solvent resistance	Quality control
Urethane coating	Process studies	Lacquers

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A wide range of urethane lacquer formulations - especially crosslinked, cure-in-place urethanes - were studied and evaluated as topcoats for the Army's New Protective Mask. Excellent optical clarity, excellent flexibility, and excellent solvent and abrasion resistance were all obtained, but not all in the same formulation. Work is continuing in follow-on contract DAAK11-77-C-0007.

410452

DD FORM 1473 1 JAN 73   EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-LF-014-6601

PREFACE

This Final Report was submitted by Utility Research Company, Montclair, New Jersey, under Contract DAAA15-76-C-0136, with the Chemical Systems Laboratory, US Army Armament Research and Development Command. Mr. J. Mok was the Contract Project Officer. Work was carried out from June 1976 to February 1977.

Reproduction of this document in whole or in part is prohibited except with permission of Director, Chemical Systems Laboratory, Attn: DRDAR-CLJ-R, Aberdeen Proving Ground, Maryland 21010; however, Defense Documentation Center is authorized to reproduce the document for US Government purposes.

The use of trade names in this report does not constitute an official endorsement or approval of the use of such commercial hardware or software; this report may not be cited for purposes of advertisement.

When Government specifications or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished or in any way supplied the said specifications or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

The information in this document has not been cleared for release to the general public.

PRECEDING PAGE BLANK-NOT FILMED

TABLE OF CONTENTS

A STUDY ON OPTICALLY TRANSPARENT POLYURETHANE COATINGS
FOR THE NEW PROTECTIVE MASK

1. INTRODUCTION AND SUMMARY

This document is the Annual Report on laboratory developmental studies of optically transparent polyurethane coatings for the New Protective Mask and the Final Report on Contract DAAA15-76-C-0136.

The objectives of this program were to improve the mask coating and the coating application process, and to assist the production coating contractor, AYO Company, in solving emergent process problems. Major effort was devoted to the elimination of optical defects known as "gel spots" that appeared in the coating in an unpredictable manner, by elaborate filtration, ultracentrifugation, fractional precipitation entrainment, and the institution of semi-cleanroom procedures in the coating room. The origin of the spots was never completely determined; but the problem was largely abated by meticulous cleanliness in the handling of the coating solutions, and good quality coatings were obtained. The coating contractor was also furnished with quality control and test methods such as determinations of viscosity and solids content, and with a method for casting a urethane film onto release paper to give an unsupported film for "gel spot" examination.

Major effort was also devoted to formulating new urethane topcoatings with improved solvent and abrasion resistance, based on two-component, cure-in-place systems, UV-curing systems and moisture-catalyzed systems. In general, excellent solvent and abrasion resistance, excellent optical properties, and excellent flexibility could be obtained - but not all at the same time. Systems with good solvent resistance, for example, tended to be inflexible and/or to exhibit poor optical properties, particularly when flexed. However, steady progress was made; and the best formulations at the end of the program were dramatically better in all respects - including combinations of properties - than the best formulations at the beginning of the program. The work is continuing in a follow-on program - Contract DAAK11-77-C-0007 - and progress can be followed in the Monthly Reports of that contract.

Major effort was also devoted to liaison. Contacts were established with all of the urethane coating manufacturers, and frequent discussions were held with those few who had products that appeared to hold promise for this application. Close liaison was also maintained with the Edgewood Mask Management Office and with AYO Company, with frequent reciprocal visits, in order to implement all advances as soon as possible.

The encouragement of Messrs. Charles Shoemaker and Josiah Mok of the Edgewood Mask Management Office and of Mrs. Anita Young and Mr. Martin Greshes of AYO Company is gratefully acknowledged.

2. OPTICAL DEFECTS IN MASK DIP COATINGS

Silicone rubber gas masks coated with a urethane film by dipping into a solution of urethane polymer in toluene/isopropanol frequently exhibit optical defects variously characterized as "gel spots", "dimples", etc.; and efforts to eliminate them have been rather inconclusive.

2.1 Description of the defects

The spots look at first glance like dust or dirt specks, and indeed some of them appear to be only dust held on the surface by electrostatic attraction and can be washed off. But others appear to be embedded in the film if not actually part of the film itself. Under a low power microscope, some of the spots look like embedded fibers or lint, and probably are. Others look like ragged chunks of glass or polymer and may be sticking out of the surface of the film and/or lying in a depressed crater in the film surface. Some look like trapped bubbles, and may be; and still others look like the "fish eyes" that occur in polymer solutions when small, undissolved, cross-linked particles are present.

The spots are in some way related to the properties of the silicone rubber substrate. In a demonstration experiment, a coating bath which was giving excessive spotting on silicone lenses gave few if any spots on a CR-39 plastic lens and absolutely no spots at all on a four inch square glass plate. The coated glass was so optically perfect that it was necessary to scratch it with a knife point to convince people that it was indeed coated.

The spots do not interfere appreciably with vision; but they mar the appearance of a brand new mask, and they call into question the degree of control of the manufacturing process; so they are decidedly not acceptable.

2.2 Filtration trials

When a solution contains suspended particulates, the obvious thing to do is to filter it; but the coating contractor (AYO Co.) found that filtration through four layers of Whatman filter paper failed to improve the quality of the coatings, and Utility Research Company found that filtration through special metal filters developed for filtering polymer solutions also failed. Accordingly, a batch of coating solution known to be giving spots was percolated slowly through an eight-inch column of glass wool which had been coated with a silanizing primer designed to enhance the adhesion of polymers to silica surfaces. It was reasoned that the primer coating, along with the great bed depth and the slow percolation offered the best possible chance to remove any suspended matter, particularly any polymer gels.

The coating bath percolated through the column without difficulty and came out markedly brighter than it went in. The unfiltered bath showed a very stong Tyndall beam and exhibited a large number of suspended particles some of which looked like dust and some of which looked like fibers. The filtered bath

- 8 -

still showed a Tyndall beam (it was after all a colloidal system and would be expected to show some Tyndall effect), but it exhibited almost no lint-like particles. One could see a number of points of light with a strong angular dependence; and that implied the presence of very tiny particles, perhaps dust, with dimensions comparable to the wavelength of light. There was nothing visible which could possibly cause spots of the size that cause rejection of coated lenses. In the metal coating tank, the filtered coating bath looked limpid to the eye; and there was no sign of any suspended particles including dust or fibers.

But a toroidal silicone lens coated in the freshly-filtered bath had more spots than ever.

A number of conventional and advanced polymer filters were tried in a further attempt to remove suspended particulates. Filters tried included:

- o Fluid Dynamics metal filters 0.01-inch thick and with pore sizes on the order of 3 to 5 microns.

- o Pall Corporation metal fiber filters with 3-micron pores, and a Pall Ultipore DFA-ARP filter with a rating of 0.2 micron.

- o Millipore microporous Teflon membranes with pore sizes down to about 0.5 micron.

Since the coating line was in general not available for filter evaluation, the filtered urethane solutions were evaluated by casting a 1-mil film by knife-coating the solution onto release paper and picking up the dried film on a cardboard or plastic frame, then looking for and counting the spots. All of the solutions, filtered and unfiltered, gave films with large numbers of spots; and none of the filtration treatments resulted in appreciable improvement.

2.3 Ultracentrifugation trial

Approximately 2.5 gallons of Wilmington GD-102 urethane solution from AYO was taken to the Electro-Nucleonics Laboratories, Inc., Silver Spring, Md., and centrifuged at 20,000 and 53,000 RPM - a process which is routinely used there to separate viruses from aqueous suspension. The product was collected in bottles which had been not only pre-washed but also rinsed with centrifuged solution which was then re-cycled. Samples were collected of 20,000 RPM centrifugate, 53,000 RPM centrifugate and centrifuge "bottoms" containing the separated particulates. Light beam examination indicated that the centrifuged material was significantly cleaner than the feed, but some residual fine suspended material could still be seen in the Tyndall beam.

Film casting done on the spot in a laminar flow hood revealed that all the samples gave defect spots without any appreciable difference among samples. The centrifuged material was returned to AYO for mask coating tests, but a final evaluation has not been made.

- 9 -

2.4 Fractional precipitation trials

On the hypothesis that the coating solution contains suspended particles of high molecular weight polymer too similar in density to settle or centrifuge out, too similar in refractive index to be seen, and too extensible to be filtered out - but which show up as bumps in the film when the coating solution is used as a lacquer, an attempt was made to sweep the solution with a precipitating gel as cloudy water is swept in municipal water supply plants with aluminum hydroxide gels.

Three formulations with compositions falling just inside the boundary of the two-phase region of the chart on the next page were made by diluting Spencer Kellogg XP-2506 (a material essentially equivalent to Wilmington Helastic GD-102 and available at Utility Research Company) with the requisite amount of isopropanol under sufficient agitation to achieve complete solution in less than ten minutes. Initially, all three solutions were bright and clear; but soon a thin gel of precipitated high-molecular-weight polymer formed homogeneously throughout the volume of the solutions and settled to the bottom of the bottles, entraining and carying down any suspended gel or other particles into the lower phase. Overnight, each bottle separated into two approximately equal volume phases with the compositions indicated on the diagram. The *lower* phase composition is indicated by the *upper* circled region on the diagram, since that is the one with the higher specific gravity.

The upper phases from all three test bottles were carefully decanted and combined, as were the three bottom phases; and each was then diluted as shown on the phase diagram to make casting lacquers.

The film from the 10% solids lacquer from the combined *heavy* phases was quite thick and contained a large number of prominent "gel spots". The 10% lacquer was diluted to 5%, and a thinner film resulted; but is still contained an unusual number of prominent "gel spots".

The combined *light* phases were diluted to 5% solids content, and a film was cast. This was one of the cleanest and best films seen on this project, with only a few, scattered blemishes that may well have been merely tramp dust. Enough untreated XP-2506 was then added to raise the solids content to 10%, and a final film was cast. It was noticeably poorer than the 5% film.

No mask coating facilities were available for a full scale test of the fractional precipitation process.

2.5 Solvent reformulation trials

Most commercial lacquer formulations contain at least three different solvents, of progressively slower evaporation rate. The fastest one gives a quick set, the next one gives drying with time for leveling, and the final one one gives plasticization during the final hardening process. A simple illustration
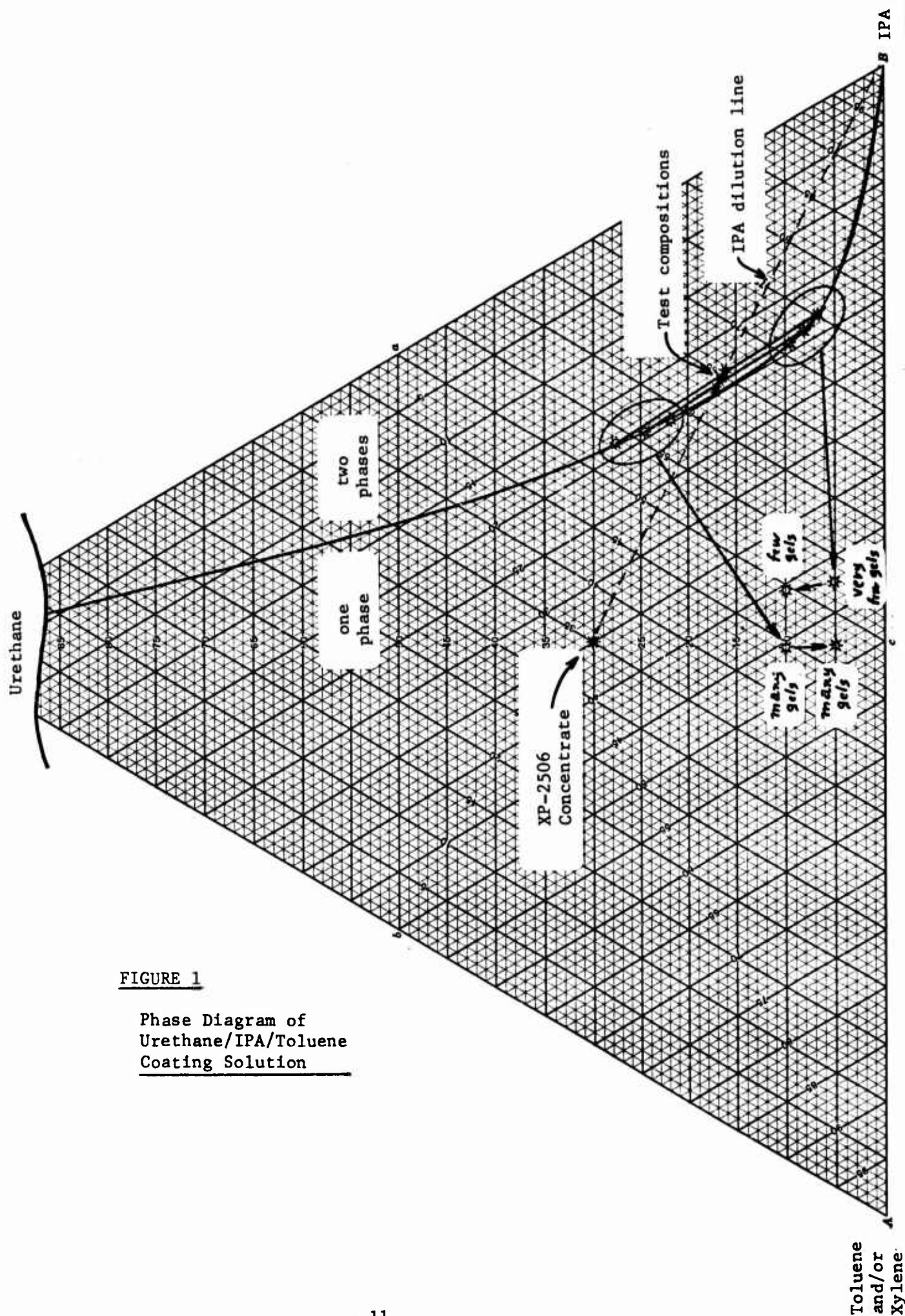
FIGURE 1

Phase Diagram of
Urethane/IPA/Toluene
Coating Solution

of the importance of evaporation rate to optical properties is the finding by painters of automobiles and other industrial items that require a glossy finish that they obtain a dull finish on humid days; so it is standard practice to add a "retarder" to the paint then. With transparent lacquers, the solvent sequence also exerts a strong effect on such properties as haze, cloudiness and wrinkling. This aspect has had little attention from urethane coating suppliers because critical optical properties are not normally required for most urethane applications such as floor lacquers and the treatment of leather and synthetic leather products to produce the shiny "wet" look.

Scouting experiments with Wilmington Helastic GD-102 have indicated that the addition of about 5 to 10% of a slower evaporation component such as cellosolve acetate or cyclohexanone can lead to a better quality film, *i.e.*, a coating with less tendency toward haze and fewer gel particles. The addition of 5% methylisobutylketone and 2% cyclohexanone to the usual 50/50 toluene/isopropanol solvent of GD-102 also seemed to improve the clarity and lessen the number of gel particles.

A thorough and methodical study of solvent blends was not carried through and is not recommended pending a final selection of a polymer system. The properties of one urethane system differ from those of another, and they affect the solvent blend requirements considerably.

2.6 Uneven surface wetting

There is some, although inconclusive, evidence that the surface of the silicone rubber wets unevenly in the coating bath; and such a phenomenon could well result in uneven coatings. Toluene, THF, and to a lesser extent isopropanol all wet the surface of a flat silicone rubber sheet unevenly, and produced visible spots reminiscent of the "gel spots". They were not identical to the "gel spots"; they tended to be depressions or poorly-wetted spots, whereas the "gel spots" usually look like bumps. But they had the pattern of the "gel spots", and they certainly revealed the existence of regions with different wetting properties on the same sheet. Toluene, a swelling solvent for silicone rubber, produced more spots than the coating bath (which contains a toluene/IPA mixture) did; and THF, a strongly swelling solvent for silicone rubber, produced the most spots of all. After drying, the THF-treated sheet still showed spots; and now they looked like bumps. The spots from all the other solvents disappeared upon drying.

On the hypothesis that the two components of the silicone rubber might be incompletely blended in the molding step so as to leave inhomogeneities in the finished surface, three experimental moldings were made up, one with standard blending, one with ten times as much blending, and one with one-fourth as much blending. All three gave indistinguishable results in wetting tests.

These inconclusive results have left a suspicion but not a conviction, and the only firm recommendation emerging from them is to give the mask adequate soaking time in the coating bath so that any uneven wetting will have time to equilibrate.

2.7 Room cleanliness

There are other coating blemishes besides "gel spots". Some of them look like tramp dust, and some of them look like tramp fibers, both perhaps from the air. The air is indeed a likely source, since the coating laboratory is in no way a cleanroom. At the beginning of this project, the laboratory was crowded with people wearing street clothes and smoking cigarettes. There were stacks of paper towels, Kim-Wipes and glass fiber insulating batts lying around. The ceiling was Celotex panels which were visibly shedding fibers and dust. The air was vigorously circulated by a household air conditioner without a filter. There was dust on the floor and on the shelves. There was a drying oven which generated paper particles from the cardboard chambers used in it, and aerosols were generated and blasted into the atmosphere by the air jet used to dry freshly-washed lenses and masks. In view of the strong electrostatic tendencies of silicone rubber articles, it would be surprising if they did *not* pick up dust and fibers.

The above observations should not be taken as criticism of the housekeeping. The coating laboratory was quite clean by normal laboratory or production shop standards; it was dusty only by cleanroom standards. But clean-room standards are probably the ones necessary for this program.

At this writing, the coating laboratory is still not a cleanroom, but it is dramatically improved. Personnel are kept to a minimum, smoking is pro-hibited, the ceiling is sealed with plastic sheeting, the air conditioner is filtered, and the place has been generally picked up and cleaned up. It is about as dust-free as any ordinary laboratory can reasonably be. All coating solutions are pressure-filtered continuously; and a filtered-air, laminar-flow, work station is installed for the most critical operations.

A three-station, class 100 cleanroom, series of HEPAfilter, laminar-flow, work stations is planned for the developmental coating line which is under construction at this writing.

2.8 Status and conclusions

At this writing, the masks and lenses coated at AYO Co. are remarkably free of "gel spots" and dust and lint; but the reason is not satisfyingly clear. They are filtering very carefully, but even more careful filtering in test cases failed to improve the spotting. They have cleaned up the coating work station dramatically, but the improvement in the coatings did not coincide very well with the improvement in cleanliness. The suspicion persists that we have not found the real cause of the "gel spots". They may have been due, for example, to a bad batch of Helastic or an unsuspected additive in the silicone gumstock or an impurity in one or more of the solvents. Or something else that abated spontan-eously before we found it. The situation suggests that the basic procedure is sound and that the current level of cleanliness is adequate, but that the process is vulnerable to a recurrence of whatever happened before.

3. IMPROVED COATING FORMULATIONS

By far the majority of the effort on this program has been devoted to developing improved urethane coating formulations, with the objective of achieving good resistance to solvents and chemicals encountered in the field while retaining good clarity, flexibility and abrasion resistance.

The required properties may be summarized as follows:

(a) Excellent surface abrasion resistance.

(b) Excellent optical properties, including light transmission, clarity, surface smoothness, etc.

(c) Excellent chemical resistance, in particular to several test materials such as Cutter's Insect Repellent (ethyl toluamide), Decontamination Solvent No. 2, gasoline and acetone.

(d) Highly flexible with minimal or no clouding or crazing when flexed.

(e) Suitable for use from −40°F to +160°F.

(f) Good adhesion to silicone rubber.

(g) Non-yellowing upon long-term storage.

To date, there are coatings that are satisfactory for any one of the required properties and for some combinations of properties; however, there is as yet no coating satisfactory in all of the required properties at the same time.

3.1 Solvent-applied, fully reacted urethanes

The Wilmington Chemicals Helastic GD-102 is a good first-generation coating material, giving acceptable clarity, flexibility and abrasion resistance; but, being a fully-reacted, solvent-applied material, it is of course easily removed by such field-likely solvents as alcohol, acetone and insect repellants.

Wilmington WC-3102 is essentially equivalent to GD-102 (although it seemed less prone to "gel spots"); and its solvent resistance is accordingly no greater. Like the GD-102, it picks up a high surface electrostatic charge and attracts dust particles tenaciously. It is also rather sticky when fresh.

Spencer Kellogg DV-2503 and XP-2506 gave results also essentially equivalent to those of the Helastic GD-102; the XP-2506 especially gave good coatings. But the lack of solvent resistance was also equivalent, as would be expected of another solvent-applied material.

Millmaster Milloxane LS-295-D and LS-370-D proved much more difficult to apply and produced poor optical qualities such as an orange peel effect, and the addition of small quantities of modifying solvents such as methisobutylketone, cyclohexanone and cellosolve did not result in acceptable coatings.

Quinn OU-2626 produced a very hazy coating on silicone sheets.

The GD-102 coated silicone pieces also exhibited clouding or crazing when the coated part was flexed or bent. Irradiation of the coated part with about 10 megarads of high energy electrons improved the resistance toward flex clouding but did not eliminate the problem. The Viton rubber interlayer, when present, also appeared to lessen the problem, probably due to the high elongation of Viton rubber. Improved topcoatings will probably require high elongation.

There would appear to be little hope of finding a solvent-resistant, solvent-applied coating except perhaps among some of the newer, developmental polymers such as polybenzimidazole that are soluble only in exotic solvents such as dimethylacetamide; and full attention has been turned to cross-linking, cure-in-place polymers systems.

3.2 Cross-linkable, cure-in-place urethanes

The best hope of quick results in improving solvent resistance would appear to lie in the use of two-component, cross-linking, urethane systems, with blocked urethane polymer coatings in solution as a possible back-up approach. An ideal coating would be one which gives an optically clear film and exhibits complete resistance to solvents such as acetone, Cutter's Insect Repellant and DS-2 decon solution, as well as good bonding to the substrate, no crazing when flexed and no marring by abrasion. Systems have been found which do well in one or more of each of these properties, but there is not yet a system which is excellent in all of them at the same time. Some show good promise, and work is continuing in a follow-on contract.

Over 200 different experimental formulations and/or curing cycles have been tested, using chemical building blocks from a wide variety of sources. Among the chief components employed were:

- o General Mills G-Cure-857 (rigid) and G-Cure-868 (flexible) hydroxy acrylic resins.

- o Spencer-Kellogg Polyol-1066 and Polyol-DI-Castor resins, and Spenlite P99-50CX isocyanate.

- o Arco Chemicals Poly-bd hydroxy-terminated polybutadiene resin.

- o Wilmington Laboratories PU Resin X-159 and X-159 catalyst.

- o Rohm & Haas Acryloid AU 608 urethane resin and Paraplex G-51 plasticizer.

- o Cook Paint and Varnish Co. J-144-76 polyester urethane.

- o Red Spot Paint and Varnish Co. SL-18406 resin and SL-16616 catalyst.

o   Spraylat Coverlac resin system.

o   Mobay Chemicals Desmodur N-75 isocyanate

plus a number of other components less extensively investigated.

The main thrust of the work has been to develop maximum solvent
resistance and then modify the system to improve its flexibility and transparency
while degrading its solvent resistance as little as possible. Other than
intrinsic clarity, we have not been much concerned with the optical quality of
the coatings, since that is mostly a matter of handling technique rather than
chemistry and will respond to good technique once the chemistry is settled.

Of all the systems screened, the best basic one was an 80/20 blend
of General Mills G-Cure 867 and G-Cure 868 in combination with Mobay Desmodur
N-75 isocyanate. An 867/N-75 formulation showed excellent solvent resistance -
acetone, Cutter's Insect Repellant and DS-2 had no effect - but the film was
quite rigid. An 868/N-75 formulation was flexible, but DS-2 attacked it, leaving
the surface quite tacky. Bonding to silicone was excellent with both systems,
but both crazed unacceptably when flexed. Various ratios of the two resins were
screened, and the optimum seemed to be 80/20 with a curing cycle of at least
300°F for at least half an hour. Illustrative data are shown in the table below.

TABLE   -   SOLVENT RESISTANCE OF G-CURE COATINGS

Formulation and cure	Acetone	Insect repellent	DS-2 Soln.
G-Cure 867 + Desmodur N-75. 300°F for 1/2 hour	E	E	E
G-Cure 868 + Desmodur N-75. 300°F for 1/2 hour	G	G	G
80/20 867/868 + N-75. 300°F for 1/2 hour	G	E	E

In determining the chemical resistance of a urethane, a blue pig-
ment is added to the otherwise colorless formulation; and the pigmented form-
ulation is knife-coated onto Mylar film and/or onto silicone panels. The
cured coatings are then scrubbed with the test solvent, and any solvent attack
is easily detected visually by noting thinned areas in the colored film.
Rating standards are outlined in the "Test Methods" section of this report.
Soluble blue dyes can also be used when working with Mylar; but silicone
absorbs the dyes, and that tends to obscure color changes due to thinning of
the coating.

- 16 -

A variety of other urethane systems was screened for solvent resistance, but none was as promising as the G-Cure system:

o Spencer-Kellogg Polyol 1066 or Polyol DI Castor in combination with Spencer-Kellogg Spenlite P99-50CX isocyanate, cured at 260°F for 20 minutes onto flamed-and-primed silicone rubber strips, yielded a clear but mottled coating which crazed severely when flexed.

o Wilmington Laboratories' PU Resin X-159 with X-159 catalyst gave a clear, flexible film which cured at room temperature in 20 minutes or at 140°F in 5 minutes; but its chemical resistance was poor: Cutter's Insect Repellant and DS-2 both dissolved the coating within 5 minutes.

o Rohm and Haas' Acryloid AU-608 resin with Mobay's Desmodur N-75 isocyanate gave a clear but rigid coating. Neither acetone nor DS-2 had any effect, but Cutter's Insect Repellant left a surface ring where it had been applied. Paraplex G-51 plasticizer had a tendency to migrate out of the film and degraded the optics.

o Cook Paint and Varnish Company's "clear, flexible" polyester urethane J-144-76 system, cured onto Mylar at 220°F for half an hour and then postcured at 300°F for another half hour, showed poor solvent resistance to acetone and Cutter's Insect Repellent. DS-2 completely dissolved the coating.

o Red Spot Paint and Varnish Company's SL-18406 urethane lacquer showed good resistance to Cutter's Insect Repellent and DS-2, but was too rigid to be flexed.

o Hughson Chemicals, Lord Manufacturing Co., Chemglaze V004/catalyst.

With the G-Cure/N-75 system established as the best of those available, and with satisfactory curing conditions also established, attention was turned to attempting to flexibilize the G-Cure/N-75 system with plasticizers and/or long-chain, bifunctional polyols.

In initial experiments, 10% and 20% Carbowax and n-butyl alcohol were added to the basic G-Cure formulations, and coatings were heat cured at 320°F for 60 minutes. Solvent resistance appeared to be degraded by these additives; and the coatings themselves had poorer optical quality, with hazy, cloudy areas and nonuniform surfaces. B. F. Goodrich "Ameripol Rubber 606" imparted improved flexibility and improved abrasion resistance, as well as very good chemical resistance; but the rubber had a tendency to precipitate out of solution and produce an opaque film.
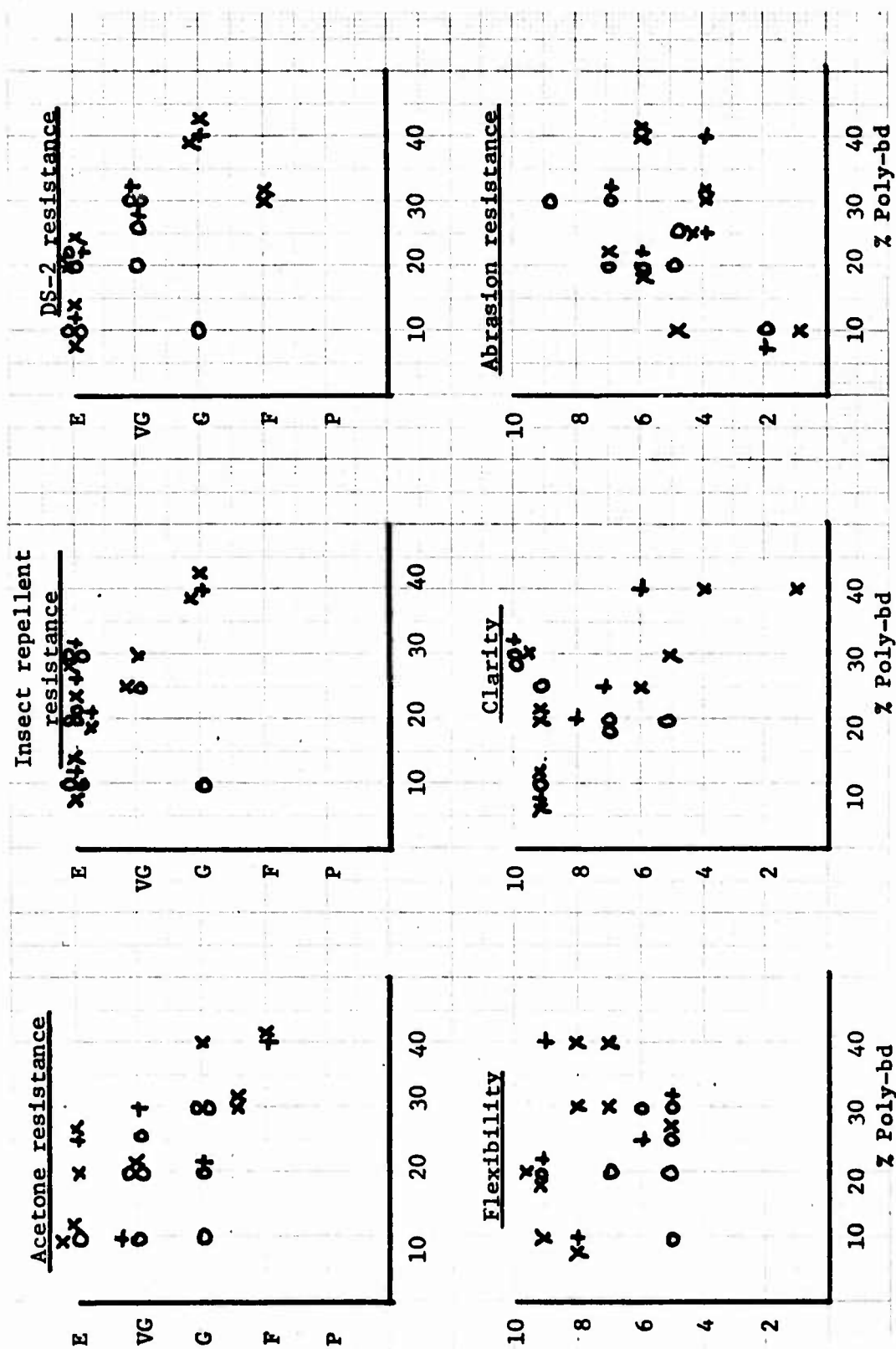
A major effort was devoted to exploring the substitution of varying percentages of ARCO Chemicals' "Poly-bd Liquid Resin", a hydroxy-terminated polybutadiene, for some of the G-Cure polyols; because scouting experiments had given rather encouraging results. Knife coatings of the G-Cure formulations with ratios of Poly-bd varying from 10% to 40% and cured at different times at the same temperature were tested to determine chemical resistance. As shown in the following figures, chemical resistance is improved at shorter curing cycles with lower percentages of the Poly-bd flexibilizer and at longer curing cycles with higher percentages of Poly-bd. Flexibility and abrasion resistance are improved with higher levels of Poly-bd; but coating clarity is degraded, often to the point of actual cloudiness. With less of the Poly-bd flexibilizer in the G-Cure system, optical clarity is improved; but flex clouding and a residual haze is seen when the strips are slightly bent. In addition, although many of the G-Cure knife coatings on Mylar had good optical clarity, the same coatings on silicone rubber often showed a haze or cloudy appearance.

The most promising results, including improved flex clouding and less residual haze, were obtained with a 5% and a 7% solids solution of the G-Cure system dip-coated onto flamed, primed silicone rubber strips and onto flamed, primed, Viton-coated strips. However, such a low percent solids solution gave an extremely thin coating; and the uniformity of the coating was questionable. Preliminary tests indicate that approximately an 0.0002-inch thick coating is deposited onto the silicone surface from a 10% solids solution of the General Mills G-Cure urethane system.

Recent study has included the moisture-catalyzed coating Chemglaze V004 from Hughson Chemicals, and it has shown the best resistance to flex clouding to date; however, this material has relatively poor resistance to the test solvents. In contrast, the General Mills G-Cure urethane has excellent chemical resistance but flex clouds when the coated silicone sample is bent. Combinations of the two coatings – Hugson V004 coated first and then a coating of G-Cure as a topcoat – gave erratic results. Preliminary indications were that an overcoat of G-Cure may improve the chemical resistance; but there were problems in obtaining a uniform overcoating, and flex clouding was still observed.

If one looks only at the *best* result obtained in each trial – a perfectly valid thing to do in exploratory work – one sees that excellent acetone resistance, flexibility, clarity and abrasion resistance have all been obtained at Poly-bd percentages ranging from 10% to 30%. Not all at the same time, but nonetheless obtained – demonstrating that it *can* be done and that further attempts to pin down the best formulations and conditions are warranted.

Inasmuch as this work is incomplete and is continuing in a follow-on program, only summary data are presented in this report. The complete, raw, data are available in the laboratory notebooks; and more complete summaries are available in the Monthly Progress Reports. Over 500 samples, including knife coatings and dip coatings on silicone rubber of the various materials discussed above are available for inspection in the Utility Research Company Laboratory.

Acetone resistance

Insect repellent resistance

DS-2 resistance

E   VG   G   F   P

% Poly-bd
10   20   30   40

Flexibility

Clarity

Abrasion resistance

% Poly-bd
10   20   30   40

% Poly-bd
10   20   30   40

Curing conditions:
15 min @ 140°F; then 40-60 min @ 260°F - O
15 min @ 140°F; then   70 min @ 260°F - +
15 min @ 140°F; then 80-90 min @ 260°F - X

Reference:
Table L1-51
Table L1-82

FIGURE 2 - Properties of [G-Cure 867 Resin + N-75 Isocyanate]
Coatings as a Function of Poly-bd Content

- 19 -

FIGURE 3 – Properties of [80/20 G-Cure 867/868 Resin + N-75 Coatings] as a Function of Poly-bd Content
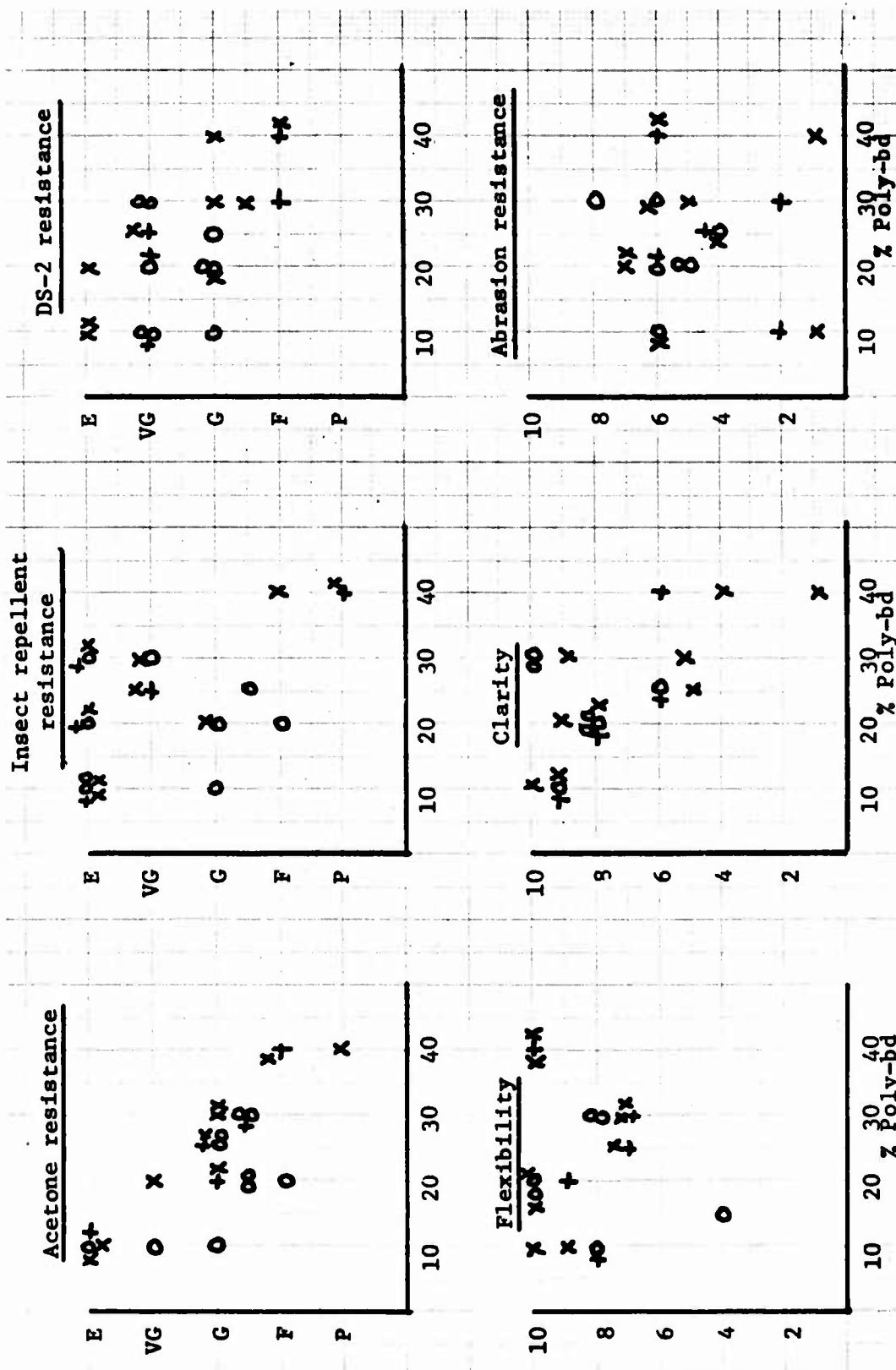
Curing conditions:

15 min @ 140°F; then 40-60 min @ 260°F –
15 min @ 140°F; then   70 min @ 260°F –
15 min @ 140°F; then 80-90 min @ 260°F –

Reference:
Table L1-51
Table L1-82

- 20 -

Another, and in some ways more promising, class of cure-in-place urethane coatings is the UV-curing system; and this approach was scouted briefly. Work was initiated with Thiokol ZM-842 (XP-9614) and ZM-883 (XP-9617) coated onto flame-treated, primer-coated, silicone rubber strips and irradiated with UV for four to six minutes. The ZM-842 products gave rigid coatings with excellent solvent resistance, while the ZM-883 product gave flexible coatings with lesser solvent resistance. Dilution with monomers to thin the formulations enough for dip-coating gave mostly brittle films with yellow discoloration. Best results were seen when the resins were used in combination: 10% ZM-842 and 90% ZM-883 in a 1:2 dilution with the monomer N-vinyl-2-pyrrolidone with 1% of the UV initiator α,α- diethoxyacetophenone plus 0.5% of 3M Fluorad Coating Additive FC-433 as a wetting agent.

Approximately 100 different formulations were applied and evaluated. Most of them gave hazy, cloudy coatings with some yellow discoloration; but others gave fairly clear, semi-flexible coatings with excellent bonding and minimal flex crazing.

Further development of this promising system was deferred to the follow-on program, partly in favor of the more immediately promising G-Cure system discussed above, and partly to allow time to set up a more powerful UV irradiation apparatus in a class 100 clean work station.

4. TEST METHODS

The test methods and rating standards used as the basis for the results reported in the foregoing sections are set forth below.

4.1 "Gel Spot" content (film casting)

A free film is cast by pouring a portion of the urethane coating solution onto Warren release paper Patent AVC1S and striking it off to 10-mils thick using a casting knife and 10-mil shims (the procedure is known as kinfe-coating). The film is allowed to dry, and then a die-cut cardboard or plastic frame carrying a border of double-sided adhesive tape is dropped onto it. The frame-and-film is lifted from the release paper, and the film is trimmed to the edge of the frame. The framed film can then be handled and examined for gel spots and other defects at one's leisure. Since the films are tacky for a while, they are best stored on edge in a slotted box like 35mm transparencies; and they should be kept in a class 100 dust-free environment until they are thoroughly dry.

4.2 Solids content of coating baths

Non-volatiles are determined gravimetrically by evaporating a sample to constant weight in a tared aluminum weighing dish. The sample itself is weighed by difference out of a small weighing bottle rather than directly in the evaporation dish in order to avoid loss of the very volatile solvents during the weighing process.

4.3 Solvent resistance of cured films

This is a somewhat qualitative and subjective test. A drop of the test solvent is placed on the surface to be tested and allowed to remain for ten minutes if it will. If evaporation takes place, more solvent is added so as to keep the surface wetted with the solvent continuously. The spot is then rubbed with a Q-tip to determine the effect on the surface.

Rating system:

Excellent - No detectable effect.

Good   - Slight defect such as surface tack or residual ring.

Fair   - Some but not all of the coating can be rubbed off after ten minutes.

Poor   - Quick coating attack and easy rub-off.

Very poor - Immediate coating dissolution.

4.4 Flexibility

A subjective rating useful mostly for immediate comparisons. A sample on Mylar film or a silicone rubber strip is bent or flexed gently or sharply and the result noted. A rating of "1" indicates a rigid, brittle material; and a rating of "10" indicates a highly flexible, rubbery material.

4.5 Clarity

A one-to-ten rating system wherein "1" indicates an extremely cloudy or badly discolored material, and "10" indicates an optically clear material.

4.6 Abrasion resistance

The sample is rubbed vigorously with a pencil eraser, wiped with a paper towel, and examined for damage. "10" indicates that no mark is left, while "1" indicates a marred, scratched, cloudy surface.

4.7 Film thickness

The object being coated (*e.g.*, a mask or a silicone rubber panel) is weighed accurately, coated and reweighed. The weight gain is the weight of the coating; and the weight of the coating divided by the measured area of the object gives the weight of coating per unit area, which is a direct measure of the average coating thickness. The method will not detect thin areas in an otherwise adequate coating, but it serves as a check on the constancy of the overall coating process.

DISTRIBUTION LIST

Administrator
Defense Documentation Center
Cameron Station
Alexandria, Va. 22314
　　　　Attn:　Accession Division......................... 2 copies

Commander
U.S. Army Armament Material Readiness Command
　　　　Attn:　DRSAR-RDT.................................. 1 copy

Commander
Chemical Systems Laboratory
Aberdeen Proving Ground
Maryland 21010
　　　　Attn:　DRDAR-CLJ-L................................ 3 copies
　　　　Attn:　DRDAR-CLJ-R................................ 3 copies
　　　　Attn:　DRSAR-MAS-C................................ 1 copy
　　　　Attn:　Mr. J. Mok, DRDAR-CLW-P.................... 12 copies
　　　　Attn:　DRDAR-CLD.................................. 1 copy
　　　　Attn:　DRDAR-CLW.................................. 1 copy